

CATALYTIC ACTIVITY OF NANOPHASE METALS PREPARED SONOCHEMICALLY

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INTRODUCTION

The chemical effects of high intensity ultrasound arise from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid, which generates a transient, localized hot spot (1, 2). The local conditions reached have temperatures of ~5000 K, pressures of ~1800 atm, but with cooling rates that exceed 10^{10} K/s (3, 4). We have made use of these extreme conditions to develop a new technique for the synthesis of nanostructured heterogeneous catalysts. When irradiated with high intensity ultrasound in low volatility solvents under argon, volatile organometallic precursors produce high surface area solids that consist of agglomerates of nanometer clusters. These nanostructured solids are active heterogeneous catalysts for hydrocarbon reforming and CO hydrogenation. For Fe and Co, nanostructured alloys can be formed of any composition. Using polymeric ligands or oxide supports, the initially formed nanoscale clusters can be trapped as colloids or supported catalysts, respectively.

A central focus of recent work in materials chemistry has been the preparation of nanostructured materials (5, 6). A variety of chemical and physical preparative methods have been applied to produce materials with nanometer structure; these include metal evaporation (7), decomposition of organometallic compounds (8), and the reduction of metal salts (9, 10). Sonochemical decomposition of transition metal carbonyl compounds has also been proven to be a useful technique to generate nanophase transition metals (11, 12).

One of the advantages of our sonochemical synthesis of nanostructured materials is that various forms of nanophase materials can be generated simply by changing the reaction medium. When precursors are sonicated in high boiling alkane such as decane or hexadecane, nanostructured powders are formed. Using a polymeric ligand (e.g. polyvinylpyrrolidone (PVP)) or inorganic support (silica, alumina, etc.), nanophase metal colloids and nanostructured supported metal catalysts are generated (Scheme 1). A transmission electron micrograph of the nanocolloid Fe/PVP is shown in Figure 1.

EXPERIMENTAL SECTION

All manipulations for the preparation of samples were performed using Schlenk vacuum line and inert atmosphere box (Vacuum Atmospheres, < 1 ppm O₂) techniques. Pentane was distilled over sodium-benzophenone. Decane and hexadecane were distilled over sodium. Ultrasonic irradiation was accomplished with a high intensity ultrasonic probe (Sonic and Materials, model VC-600, 1 cm Ti horn, 20 kHz, 100 Wcm⁻²).

X-ray powder diffraction data were collected on a Rigaku D-max diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). Scanning electron micrographs were taken on a Hitachi S800 electron microscope. Transmission electron micrographs were taken on a Phillips CM-12 electron microscope. Samples for elemental analysis were submitted in sealed vials without exposure to air.

Hydrogen (99.99%, Linde), methane (99.97%, Matheson) and CO (99.0+%, Linde) were further purified through 5 Å molecular sieves and oxy-traps (Alltech). Cyclohexane (99+%, Fischer) was dried over molecular sieves prior to use. In cyclohexane reaction, a MKS mass flow controller maintained the flow of hydrogen at 27.5 cm³ (STP)/min to carry the cyclohexane vapor at a constant partial pressure of 0.1 bar through the catalyst. A quartz reactor was used for both adsorption and gas-solid catalytic studies. The catalysts were transferred from an inert atmosphere box to the catalytic rig without exposure to air. Surface areas were calculated by applying the BET equation to the N₂ adsorption isotherm measured at 77 K. The gas products obtained during the temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) experiments were analyzed by a quadrupole mass spectrometer (Spectra Instruments). The catalytic reaction products were analyzed by gas chromatography (Hewlett-Packard 5730A) on a n-octane/Porasil C column with flame ionization detector.

RESULTS AND DISCUSSION

Synthesis and catalytic studies of nanostructured silica-supported Fe

Ultrasonic irradiation of decane solutions of iron pentacarbonyl, Fe(CO)₅, in the presence of silica gel produces a silica-supported amorphous nanostructured iron. Silica gel (Universal Scientific Incorporated chemicals, 63-100 mesh) was pretreated at 450°C under vacuum (1×10^{-5} Torr) for 10 hours before use. A solution of Fe(CO)₅ in dry decane was added to this, and the slurry was irradiated at 20°C with a high-intensity ultrasonic probe for 3 hours under argon. After irradiation, the black powder was filtered and washed with dry pentane in an inert atmosphere box. The iron loading on silica can be easily varied by

changing the initial concentration of the $\text{Fe}(\text{CO})_5$ solution. Elemental analysis reveals Fe, Si, O and a trace amount of carbon (<1%) to be present. The origin of carbon most likely arises from the decomposition of CO or the alkane solvent during ultrasonic irradiation. Conventional silica-supported crystalline iron catalysts were prepared using the incipient wetness impregnation method by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in an aqueous solution containing silica gel. These samples were dried at 220°C for 12 hours, and calcined at 450°C under an O_2 flow for 1 hour. Reduction of iron supported on silica was carried out in a flow of hydrogen for 1 hour at 200°C, for 1 hour at 300°C, and finally for two hours at 450°C.

Transmission electron microscopy shows that the iron particles produced by sonolysis of $\text{Fe}(\text{CO})_5$ were highly dispersed on the silica surface. The iron particles range in size from 3 to 8 nm. Chemisorption of CO allowed measurement of the dispersion and the average particle size of the iron supported on the silica surface (13). CO chemisorption measurement data at -78°C show the average iron particle size to be ≈ 7.3 nm, which corresponds well with TEM data.

The catalytic activity of the silica supported nanostructured iron was probed in the commercially important Fischer-Tropsch synthesis reaction (i.e., hydrogenation of CO). Figure 2 compares the activity (in terms of turnover frequency of CO molecules converted per catalytic site per second) of silica-supported nanophase iron and conventional silica-supported iron (prepared by the incipient wetness method) as a function of temperature. These catalytic data were obtained at high iron loading and low dispersion to minimize the effects of support and dispersion. The sonochemically produced iron on silica catalyst is an order of magnitude more active than the conventional supported iron. Moreover, the silica-supported nanostructured iron catalyst exhibits high activity at low temperatures (<250°C), whereas the silica supported conventional iron catalyst has no activity. We suggest that the dramatic difference in activity between the two samples below 300°C may be due to the amorphous nature of iron and the inherently highly-defected surface formed during sonolysis of $\text{Fe}(\text{CO})_5$ when the amorphous state of iron is preserved. Above that temperature the activity of our sonochemically prepared catalyst declines, which may be due to crystallization, surface annealing, and deactivation of the catalyst as result of surface carbon deposition.

Differences between the catalytic properties of the nanostructured iron and of conventional supported catalysts are also observed in selectivities of hydrocarbon synthesis. Under our conditions, the major reaction products for both catalysts are short chain C_1 - C_4 hydrocarbons and CO_2 . Product distribution of hydrocarbons showed that at temperatures lower than 275°C, the silica-supported nanostructured iron catalyst shows higher selectivity towards long chain hydrocarbons (C_5), whereas the conventional supported iron shows no activity at these temperatures. At temperatures higher than 275°C, the reaction product distributions are similar for both types of catalysts.

Synthesis and catalytic studies of nanostructured Fe-Co alloys

$\text{Fe}(\text{CO})_5$ and $\text{Co}(\text{CO})_3(\text{NO})$ were chosen as precursors because of their high vapor pressures at modest bulk solution temperatures where they are still thermally stable. Solutions of $\text{Fe}(\text{CO})_5$ and $\text{Co}(\text{CO})_3(\text{NO})$ at various relative concentrations in dry decane were irradiated at 0°C with a high-intensity ultrasonic probe for 3 hours under argon. After irradiation, a black powder was formed, which was filtered and washed with dry pentane in the glove box. The composition of the Fe-Co alloys can be controlled simply by changing the ratio of solution concentrations of the precursors; any alloy compositions ranging from pure Fe to pure Co can be readily obtained.

The solid-solution nature of the alloys was confirmed by TEM-EDX results, which were made on different spots of the polycrystalline alloy powders. The EDX results show that the alloys are homogeneous on a nanometer scale. The original Fe, Co, and Fe-Co alloys produced by ultrasound are porous, coral-like agglomerates of few-nanometer sized clusters; they are structurally amorphous on the nm scale, as determined by XRD, electron-beam microdiffraction, and DSC. After heat treatment under H_2 gas flow at 400°C for 2 hours, all samples underwent an irreversible crystallization, as shown by both DSC and XRD. The XRD results show no peaks attributable to iron/cobalt oxide, iron/cobalt carbide or other iron/cobalt impurity phases. Pure Fe crystallizes to cubic (bcc) structure, pure Co crystallizes to cubic (fcc) and hexagonal (hcp) mixed structures. All the alloys that we have tested so far crystallize in the bcc structure, which is consistent with the known Fe-Co equilibrium phase diagram (14). Elemental analysis results show that nearly pure metal and alloys are produced. SEM at high magnification indicates that these materials are porous aggregates of small clusters of 10-20 nm particles. Surface electronic structures and surface compositions of the sonochemically prepared Fe-Co alloys were also examined by using x-ray photoelectron spectroscopy (XPS). The XPS measurements have been performed on heat treated samples before catalytic reactions. The electronic structures of the surfaces of these samples appear to be the same as the pure metals. The surface compositions of the alloys demonstrate some small enrichment of Fe over Co. Similar trends towards an iron-enriched surface have been reported by other researchers with other preparations using coprecipitation methods (15).

Catalytic studies of the sonochemically prepared Fe-Co alloys were made on the reactions of cyclohexane: i.e., dehydrogenation versus hydrogenolysis. These reactions provide a useful pair of structure sensitive catalytic reactions to probe the nature of the sonochemically prepared nanophase catalysts. All catalysts were treated under H_2 gas flow at 400°C for 2 hours before the catalytic studies. The catalytic activity (in terms of turnover frequency of cyclohexane molecules converted to benzene per surface Fe/Co atom per second) as a function of temperature is shown in Figure 3. Two kinds of products were formed during the

cyclohexane reaction: benzene was the only dehydrogenation reaction product and aliphatic hydrocarbons (mostly methane) were the hydrogenolysis reaction products. The catalytic selectivity (in terms of the percentage of benzene among all the reaction products) as a function of temperature is shown in Figure 4. The catalytic properties of the sonochemically prepared Fe, Co and Fe-Co alloys in the cyclohexane reaction exhibit interesting trends. First, they are all active catalysts for cyclohexane conversion: pure Co has the highest activity (albeit primarily for hydrogenolysis), pure Fe has the lowest activity, and Fe-Co alloys have intermediate activity between pure Fe and pure Co. Second, Fe-Co alloys generate much more dehydrogenation product (benzene) than pure Fe or Co. Third, the 1:1 Fe/Co alloy has both much higher dehydrogenation activities and selectivities at all reaction temperatures (250°C to 300°C) than the other alloys or pure metals. In the best cases, the selectivity for dehydrogenation approaches 100%. The origin of this dramatically improved selectivity is under further investigation.

CONCLUSIONS

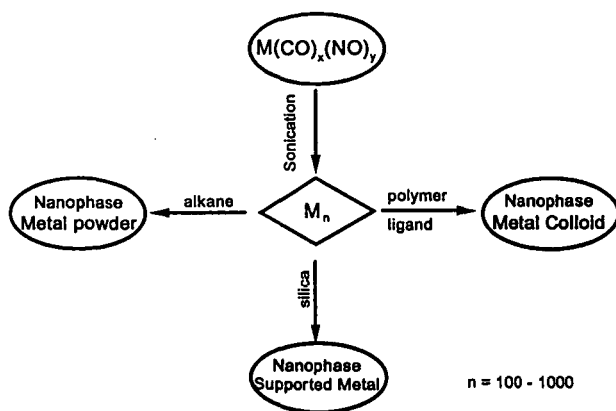
Sonochemical decomposition of volatile organometallic precursors in high boiling solvents produces nanostructured materials in various forms with high catalytic activities. Sonication of iron pentacarbonyl with silica in decane at 20°C generated supported amorphous nanostructured Fe on silica catalyst. The nanostructured Fe on silica catalyst showed higher catalytic activity for the Fischer-Tropsch synthesis compared to the conventional Fe/silica catalyst prepared by incipient wetness method. Sonochemical decomposition of $\text{Fe}(\text{CO})_5$ and $\text{Co}(\text{CO})_2(\text{NO})$ in decane at 0°C generated nanostructured Fe and Co metals and Fe-Co alloys. The sonochemically prepared Fe-Co alloys have large surface areas relative to bulk metal even after heat treatment. We find very high catalytic activity for these Fe, Co, and Fe-Co powders for the dehydrogenation and hydrogenolysis of cyclohexane. The sonochemically prepared Fe-Co alloys show high catalytic activity for the dehydrogenation of cyclohexane to benzene, with 1:1 ratio Fe-Co alloys having selectivities as high as 100%.

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Scheme 1. Sonochemical synthesis of various forms of nanostructured materials.

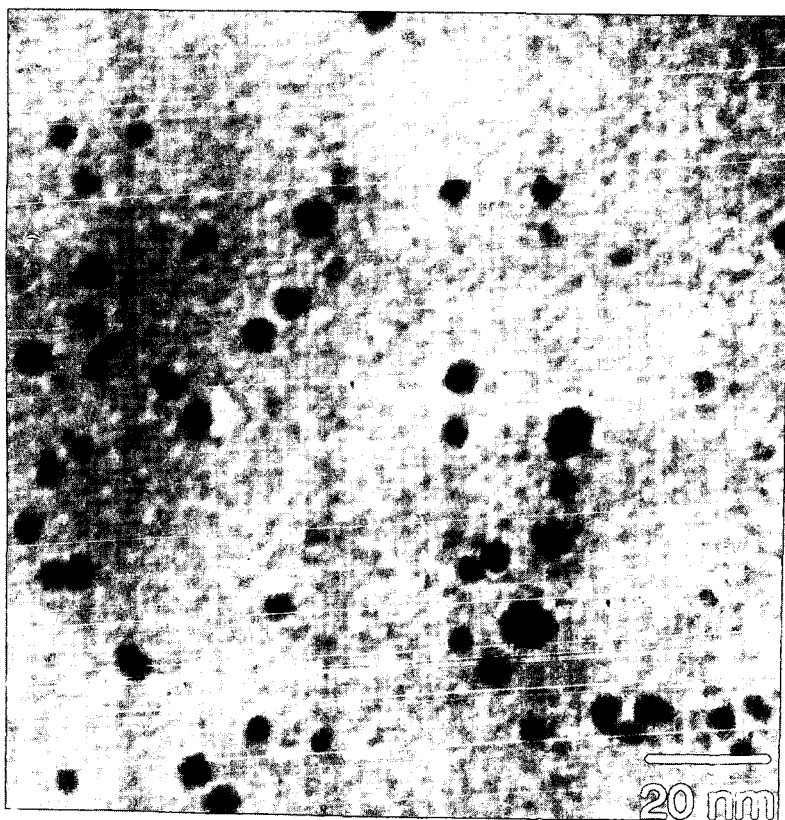


Figure 1. Transmission electron micrograph of nanostructured Fe/PVP, obtained on a Philips 420 electron microscope.

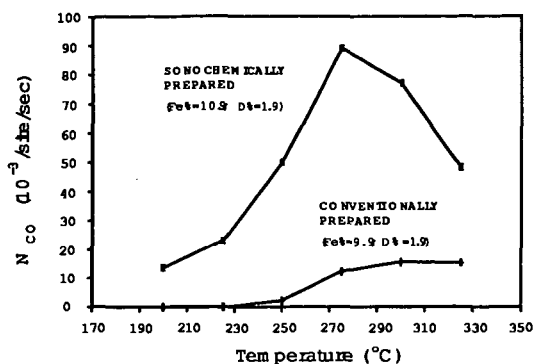


Figure 2. The catalytic activity for Fischer-Tropsch synthesis as a function of temperature. Silica-supported nanostructured iron catalyst prepared by ultrasonic irradiation of a decane solution of $\text{Fe}(\text{CO})_5$ slurried with silica (iron loading wt% = 10.94, and dispersion, D% = 1.85) compared to conventional silica-supported crystalline iron catalyst prepared by the incipient wetness method (Fe wt% = 9.91, D% = 1.86). H_2/CO = 3.48, 1 atm.

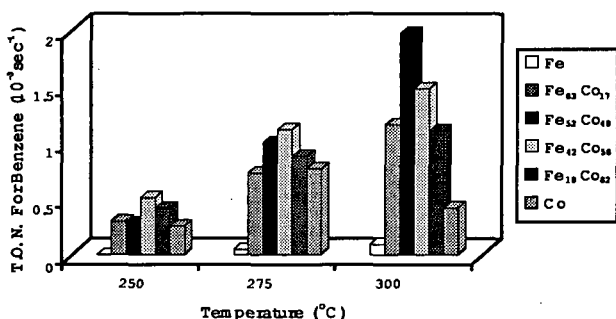


Figure 3. The catalytic activity of Fe, Co, and Fe-Co alloys for dehydrogenation of cyclohexane to benzene as a function of temperature. H_2/CO = 3.48, 1 atm.

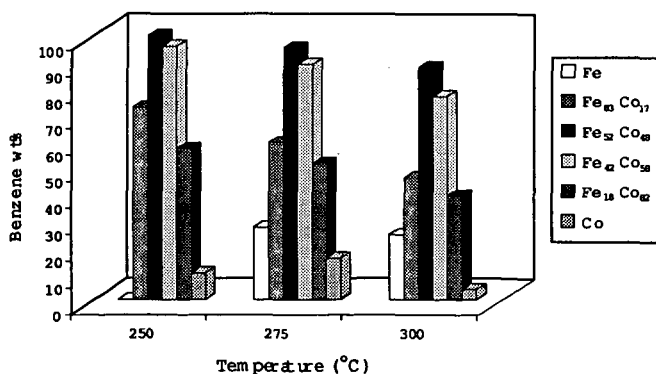


Figure 4. The catalytic selectivity of Fe, Co, and Fe-Co alloys for dehydrogenation versus hydrogenolysis of cyclohexane as a function of temperature. H_2/CO = 3.48, 1 atm.